

Synthesis and Electrical Conductivities of Fully Conjugated Schiff Base Macrocycles Containing 1,3,4-Oxadiazole

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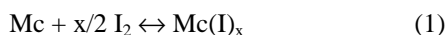
Abstract: Conjugated Schiff base macrocycles containing 1,3,4-oxadiazole were prepared by [2+2] cyclic condensation of phenylenediamine with 2,5-bis(m-formyl-phenyl)-1,3,4-oxadiazole. These macrocycles with iodine or TCNQ produced stable charge-transfer complexes. The formation of complexes were identified by UV-Vis and FT-IR spectra.

Keywords: Conjugated Schiff base macrocycles; synthesis; charge-transfer complexes.

The delocalized π -electronic planar structure of the molecule is necessary to design new organic metals. Recently much attention was paid on the use of much rigid electron-withdrawing 1,3,4-oxadiazole unit as building blocks in the synthesis of synthetic metals and organic light-emitting diodes materials¹⁻². Previously we have found the conjugated macrocycle containing 1,3,4-oxadiazole could be oxidatively doped with iodine to form a charge-transfer complex with a conductivity of $4.6 \times 10^{-2} \text{scm}^{-1}$ ³. To continue this work and understand the relationships between molecular structure and solid state properties, here we reported the synthesis and properties of other conjugated Schiff base macrocycles. We focused our attention on the formation of the complexes of macrocycles with iodine, TCNQ and their electroconducting properties.

The synthesis of the target compounds was shown in **Scheme 1**. The conjugated Schiff base macrocycles **3b-c** were synthesized in the presence of barium (II) template ion. The ¹H-NMR spectra of macrocycle **3a** was complicated, the peak at δ 4.70 ppm showed the presence of benzimidazole-type tautomer such as **6** besides conjugated Schiff base macrocycle **3a** (**Scheme 2**). Similar intramolecular cyclization was reported by us⁴ and others⁵. We used the copper (II) as template ion instead of barium (II), however the product was not macrocycle **3a** but complex **4** of bisbenzimidazole with copper (I). The copper(II) acted as oxidizing agent and was reduced to copper (I) in the formation of bisbenzimidazole⁶.

Macrocycles **3b-c** were yellow and became black and dark red respectively in colour after being doped with iodine, which indicated the oxidation of macrocycles. (**equation 1**)

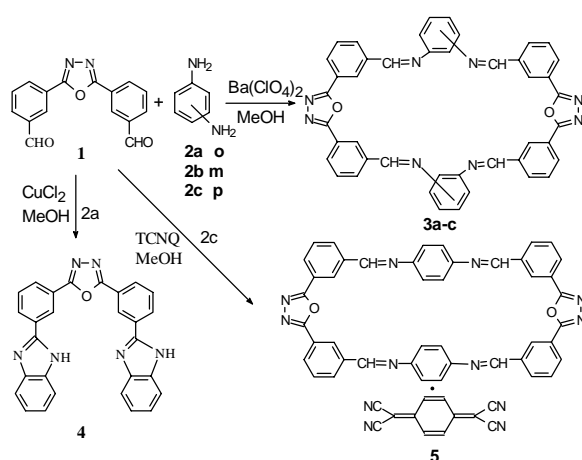


Resonance Raman spectroscopy showed that the iodine was present as I_5^- (169cm^{-1})⁷. According to the calculation (based on the weight of absorbed iodine), $x=5.15$, which indicated the formation of complexes. The conductivities of I_2 -doped macrocycles **3b** and

3c were $8.1 \times 10^{-7} \text{Scm}^{-1}$ and $1.2 \times 10^{-5} \text{Scm}^{-1}$ (four probe method) respectively.

The complex **5** of macrocycle **3c** with TCNQ was directly synthesized by the [2+2] cyclic condensation of compound **1** with 1,4-phenylenediamine in the presence of TCNQ instead of barium perchlorate (**Scheme 1**). The electrical conductivity was $2.5 \times 10^{-6} \text{Scm}^{-1}$ (two probe method). However, the complex of macrocycle **3b** with TCNQ was not obtain.

Scheme 1.



Scheme 2.

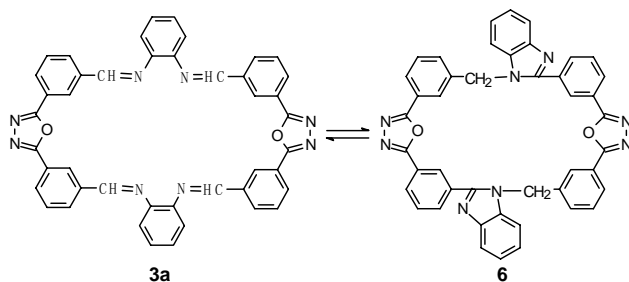
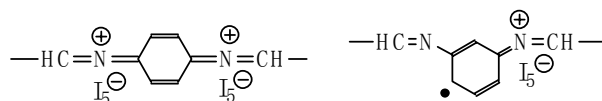


Figure 1-2 showed FT-IR spectra of macrocycle **3b-c** and their complexes with iodine. In addition to the decreasing of peak strength of macrocycle **3b** after being doped with iodine, C=N stretching at 1630cm^{-1} and the benzene ring stretching at 1581cm^{-1} as well as the peaks at 1135cm^{-1} , 970cm^{-1} and 953cm^{-1} disappeared, a new broad peak at 1609cm^{-1} was observed. To macrocycle **3c**, the strength of absorption from 1700 to 700cm^{-1} (C=N stretching and benzene ring absorption) was apparently decreased after doping with iodine. The C=N stretching in macrocycle **3c** which appeared at 1624cm^{-1} shifted to 1614cm^{-1} and a new peak at 1594cm^{-1} was observed. In addition, the peak at 970cm^{-1} disappeared. These changes were maybe related to the following structures in the formed charge transfer complexes ¹.



The UV-Vis spectra of macrocycles **3b-c** and complexes with iodine in DMF were showed in **Figure 3**. The λ_{\max} values of the macrocycle **3b** appeared at 280 nm, that of I_2 -doped macrocycle **3b** red shifted to 300 nm and a new peak at 367 nm was formed. The λ_{\max} values of the macrocycle **3c** appeared at 285 nm and 379 nm, for comparison, those of I_2 -doped macrocycle **3c** red shifted to 300 nm and blue shifted to 365 nm, respectively. These changes also attributed to the formation of polaron structures in the charge transfer complex. This result was consistent with the FT-IR analysis. **Figure 4** showed the UV-Vis spectra of the macrocycle **3c** and CTC5. The λ_{\max} value of macrocycle **3c** was at 379 nm, the one of CTC5 red shifted to 507 nm. This indicated the formation of charge transfer between the macrocycle and TCNQ. The FT-IR spectra of CTC5 exhibited $C\equiv N$ stretching vibrations at 2175cm^{-1} , which was consistent with a significant degree of charge transfer from the macrocycle **3c** to TCNQ (neutral TCNQ exhibited $\nu_{C\equiv N}$ at 2234cm^{-1})⁸. The electrical conductivity of I_2 -doped macrocycle **3b** was lower than that of **3c**, which was related to the lower planar structure and the different polaron structure.

Figure1 FT-IR spectra of macrocycle**4b** (a) and its complex with iodine (b)

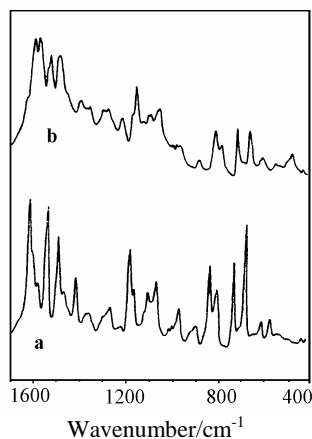


Figure2 FT-IR spectra of macrocycle**4c** (a) and its complex with iodine (b)

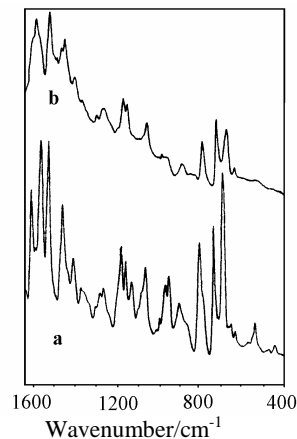


Figure 3 UV-Vis spectra of macrocycle**4b-c** and their complexes with iodine (a) **4b**,(b) I_2 -doped **4b**, (c) **4c**, (d) I_2 -doped **4c**.

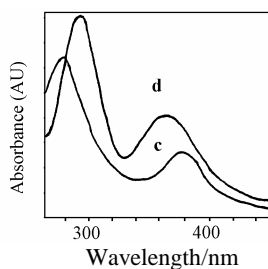
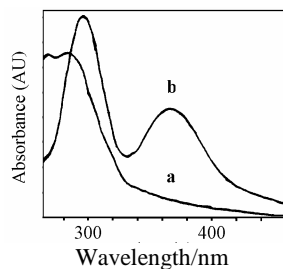
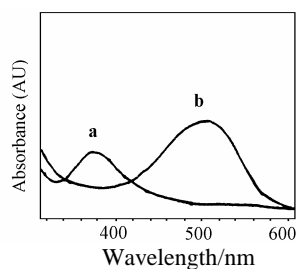


Figure 4 UV-Vis spectra of **4c**(a) and CTC6 (b)



Experimental

A mixture of compound **1**⁴ (1.08 mmol) and **2a-c** (1.08 mmol) in dry MeOH (30 ml) was refluxed until the solid dissolved completely. To this solution Ba (ClO₄)₂ (CuCl₂ or TCNQ) (1.15 mmol) in MeOH (10 ml) was added dropwise. The reaction solution was refluxed for 2 hour. The precipitate formed was filtered, washed with MeOH (10 ml x2), and then dried in vacuum at room temperature to give yellow or white powders.

3a: yield 49.3%; m.p. 276-284 °C; ν_{\max} /cm⁻¹ (KBr) 1600 (C=N); MS (FAB) 701 (M⁺+H); Found: C, 67.09; H, 4.18; N, 14.04%. Calcd. for C₄₄H₂₈N₈O₂·5H₂O C, 66.83; H, 4.84; N, 14.17%.

3b: yield 95.3%; mp. >360 °C; λ_{\max} /cm⁻¹ (KBr) 1630 (C=N); δ_{H} (TFA-d₁) 10.1 (d, 1H, CH=N), 9.74 (s, 2H, CH=N), 9.30-9.51 (m, 3H, CH=N, 2Ph-H), 9.05 (s, 1H, Ph-H), 8.65-8.85 (m, 4H, Ph-H), 8.57 (d, 4H, Ph-H), 8.30-8.45 (m, 2H, Ph-H), 8.23 (s, 2H, Ph-H), 8.05-8.14 (m, 6H, Ph-H), 7.60-7.87 (m, 3H, Ph-H). Found: C, 73.44; H, 4.28; N, 15.20%. Calcd. for C₄₄H₂₈N₈O₂·H₂O: C, 73.53; H, 4.21; N, 15.59%.

3c: yield 94.0%; mp. > 36 °C; ν_{\max} /cm⁻¹ (KBr) 1624 (C=N); δ_{H} (TFA-d₁) 10.13 (t, 1H, CH=N), 9.89 (s, 1H, CH=N), 9.78 (t, 1H, CH=N), 9.68-9.72 (t, 1H, CH=N), 9.58-9.62 (d, 1H, Ph-H), 9.45-9.51 (m, 1H, Ph-H), 9.31 (s, 1H, Ph-H), 8.91 (d, 2H, Ph-H), 8.81 (s, 2H, Ph-H), 8.57-8.63 (m, 4H, Ph-H), 8.25-8.38 (m, 6H, Ph-H), 8.08-8.16 (m, 4H, Ph-H), 7.90-7.97 (m, 3H, Ph-H), 7.75 (s, 1H, Ph-H). Found: C, 71.18; H, 4.11; N, 14.98%. Calcd. for C₄₄H₂₈N₈O₂·2.5H₂O: C, 70.86; H, 4.46; N, 15.02%.

4: yield 64.0%; m.p. > 360 °C; ν_{\max} /cm⁻¹ (KBr) 1620 (C=N); MS (FAB) 455 (M⁺+H-Cu₂Cl₂); δ_{H} (DMSO-d₆) 13.40 (br, 2H), 8.97 (s, 2H), 8.43 (s, 2H), 8.24 (d, 2H), 7.74 (s, 6H), 7.31 (s, 4H); Found: C, 51.21; H, 2.96; N, 12.49%. Calcd. for C₂₈H₁₈N₆O·Cu₂Cl₂: C, 50.84; H, 2.68; N, 12.53%.

5: yield 65.0mg, 80.0%, mp. >360 °C; ν_{\max} /cm⁻¹ 2175 (C≡N), 1624 (C=N); δ_{H} (TFA-d₁) 10.09 (s, 1H, CH=N), 9.76-9.85 (d, 2H, CH=N), 9.40-9.68 (t, 4H, CH=N, 3Ph-H), 9.28 (s, 1H, Ph-H), 8.77-8.85 (d, 4H, Ph-H), 8.32-8.57 (d, 7H, Ph-H), 8.26 (s, 4H, Ph-H), 8.08 (s, 5H, Ph-H), 7.81-7.91 (s, 3H, CH=CH), 7.51 (s, 1H, CH=CH); Found: C, 71.0; H, 4.0; N, 15.8%. Calcd. for C₄₄H₂₈N₈O₂·TCNQ·3MeOH: C, 70.8; H, 4.4; N, 16.8%.

The macrocycle **3b** and **3c** (49.2 mg) were stirred with a saturated solution of I₂ in CHCl₃ (20 ml) respectively for 24 hours at room temperature. The mixtures were filtered, washed with CHCl₃ and dried in vacuum at room temperature. The black I₂-doped macrocycle **3b** (95.0 mg) and macrocycle **3c** (95.3 mg) were obtained respectively. The doped powders and CTC **6** (50 mg) were pressed into pellets at 5000 kg/cm² respectively. The electrical conductivities were measured at room temperature by standard method. The conductivity of I₂-doped macrocycle **3b** was 8.0 × 10⁻⁷ Scm⁻¹, the one of I₂-doped macrocycle **3c** was 1.8 × 10⁻⁸ Scm⁻¹ and the one of CTC **5** was 2.5 × 10⁻⁶ Scm⁻¹.

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